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A STUDY OF SOME SUBSTITUTION REACTIONS OF DEHYDROABIETIC ACID

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William E. Sisco

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FOREWORD

A study of the reactions of dehydroabietic acid and its derivatives should lead to new uses for the common and abundant wood rosin. In attempting to extend the known reactions of dehydroabietic acid, two new reactions were tried, bromination and partial reduction of the dinitro derivative.

The primary purpose of this investigation was to prepare and isolate a bromo derivative of dehydroabietic acid. Evidence of reaction was obtained, but the isolation of a satisfactory product proved difficult.

An attempt to reduce one of the nitro groups of dinitrodehydroabietic acid produced satisfactory, although negative, results.

In carrying out this investigation it was necessary to repeat much of the earlier work and satisfactory checks were obtained.

A STUDY OF SOME SUBSTITUTION REACTIONS OF DEHYDROABIETIC ACID

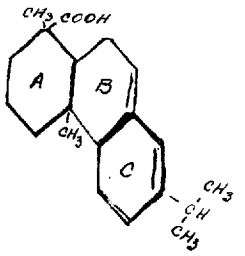
HISTORICAL

Chemical investigation of the rosin acids were first undertaken in the early part of the nineteenth century. Much of the early work had to do with the isolation of acids from different sources, and many substances of doubtful individuality were described and named in the course of the work. It gradually became recognized that the acids most suitable for the investigation of structure and properties are d-pimaric and abietic acid, which in contrast to many of the primary rosin acids, are stable or comparatively stable substances. Particular attention was directed toward the more abundant abietic acid.

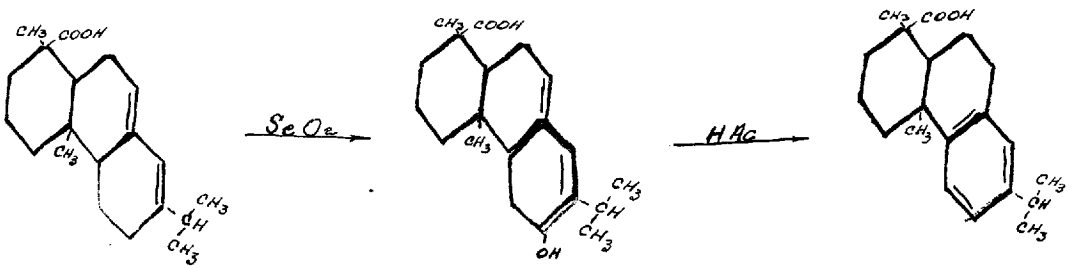
Wood rosin is known to consist largely of a mixture of isomeric acids having the molecular formula $C_{20}H_{30}O_2$. Although only a very small percent of the mixture is abietic acid, the less stable acids may be converted to the more stable abietic acid, in good yield, by a process of isomerization.

Several methods are available for this conversion. The method which is generally accepted by present day investigators was purposed by Steele (1). This method consists of refluxing a good grade of wood rosin with glacial acetic acid, followed by recrystallization of the product from ethyl alcohol.

Further investigation established the following structure for abietic acid:



With the idea of obtaining a more useful and more stable compound, Fieser and Campbell (2) made a successful attempt to aromatize ring C of abietic acid. This was accomplished by the oxidation of abietic acid to hydroxyabietic acid with selenium dioxide and dehydration of that product with glacial acetic acid:



The resulting product was called dehydroabietic acid.

Littman (3) devised a more simple method for the preparation of dehydroabietic acid. Since this was the method chosen for this investigation, it will be discussed later.

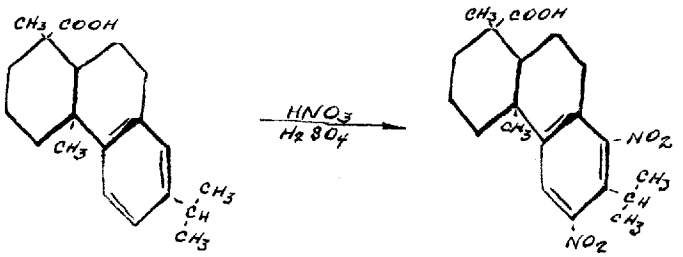
Dehydroabietic acid, then, appeared to offer the most fruitful field for investigation. This is true in spite of the difficulty involved in its preparation because it is by far the most stable acid yet prepared from rosin and because it is of a more crystalline nature.

An investigation of dehydroabietic acid and its derivatives offers certain difficulties. These are due chiefly to the complexity of the molecule, which makes difficult the successful prediction of reactions and which leads to compounds which are

difficult or impossible to obtain in crystalline form.

The presence of the aromatic ring in the nucleus of dehydroabietic acid suggested the possibility of various substitution reactions. Many of these have been tried with varying degrees of success.

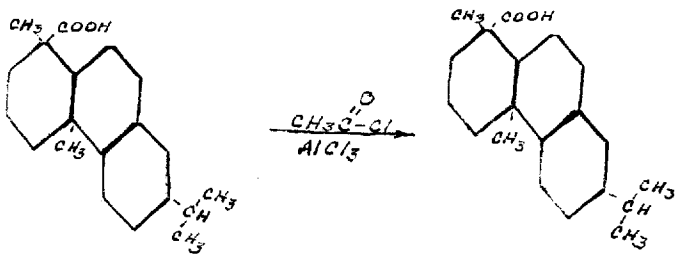
Fieser and Campbell (2) were able to obtain dinitrodehydroabietic acid by treatment of dehydroabietic acid with concentrated nitric acid in the presence of concentrated sulfuric acid.



Littman (3) was able to reduce this compound to the diamino derivative by treatment with hydrogen at 2000 pounds pressure in the presence of a copper chromite catalyst.

Hasselstrom and McPherson (4) were able to obtain a sulfonation product of dehydroabietic acid to which they assigned the molecular formula $C_{20}H_{28}O_5S \cdot 3H_2O$. No structure has been proposed.

Fieser and Campbell (5) prepared a monoacetyl derivative of dehydroabietic acid by means of the Friedel and Crafts reaction.



In a similar manner dehydroabietic acid could be assumed to undergo such a reaction as bromination. It has been the primary purpose of this investigation to determine if this reaction were possible.

Later an attempt was made to carry out a partial reduction of the dinitrodehydroabietic acid rather than the complete reduction carried out by Littman (3).

EXPERIMENTAL

PREPARATION OF ABIETIC ACID

Steele's method (1) was selected for the preparation of the abietic acid used in this investigation. Commercial Abietic Acid, donated by the Hercules Powder Company, Hattiesburg, Mississippi, was used in place of the rosin suggested by Steele.

Seven hundred grams of the Hercules Commercial Abietic Acid was dissolved in 500 cc. of glacial acetic acid and boiled for two hours under reflux. The mixture was filtered while hot and allowed to cool to room temperature. Occasional stirring was found to hasten crystallization and give finer crystals, making washing and recrystallization easier. The product was filtered and washed with successive portions of cold alcohol (nine parts by volume of 95% C_2H_5OH) until the filtrate was practically colorless.

The crude abietic acid was recrystallized four times from 95% C_2H_5OH. When crystallization was attained by cooling the mixture in an ice bath, fine crystals resulted which were more easily washed.

Four quantities of abietic acid were prepared by this proceedure and the following results were obtained:

Preparation of Abietic Acid

No.	m.p.	Yield in Grams	% Yield
1.	159-62°	121	17.3%
2.	158-61°	178	25.4%
3.	161-63° (vacuum dried)	209	29.8%
4.	159-63°	231	32.9%

In the first two runs, the acetic acid used had been purified by fractionation. The third and fourth runs were made with unpurified acetic acid. The unpurified acid may have contained some impurity which had a catalytic effect upon the isomerization. This, together with an increasing familarity with the process, may account for the successively increasing yields.

The abietic acid so prepared was set aside to be used later in the preparation of dehydroabietic acid.

PREPARATION OF DEHYDROABIETIC ACID

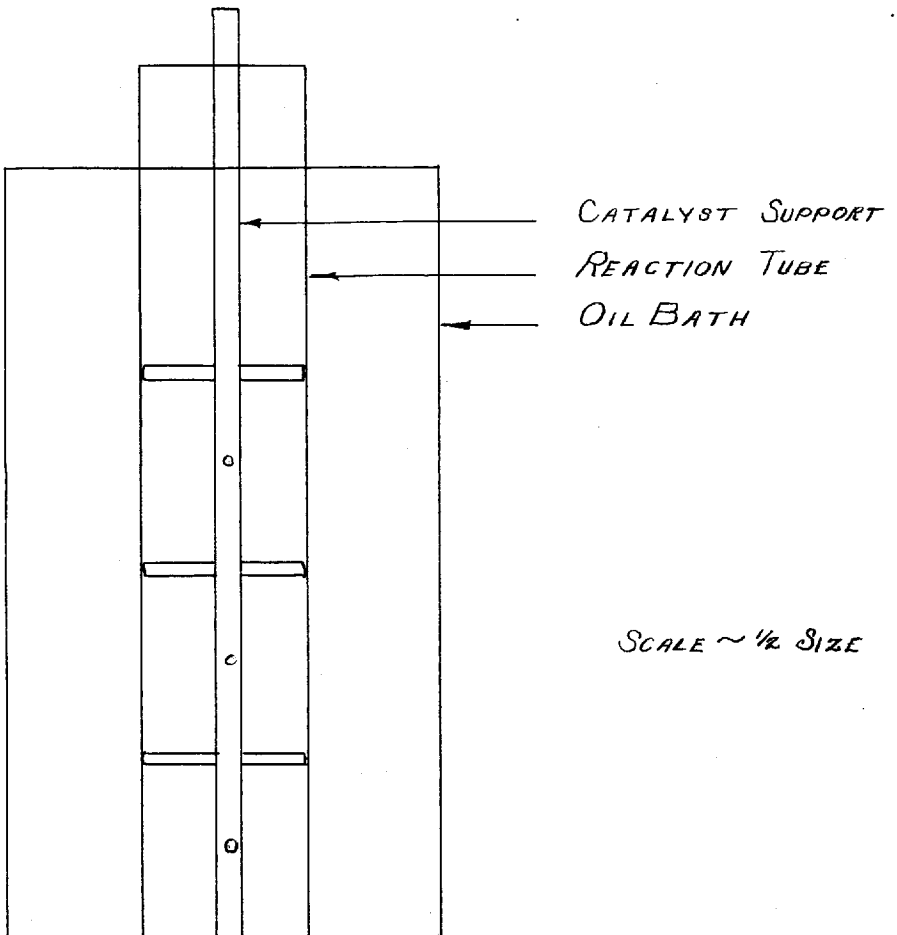
The method suggested by Littman (3) was selected for the preparation of dehydroabietic acid. This method consists essentially of the dehydrogenation of abietic acid at high temperatures in the presence of finely divided palladium. Some dihydroabietic acid is formed during the process, but this is removed by recrystallization from acetone. The dihydroabietic acid may be recovered from the filtrate after crystallization.

The catalyst used consisted of finely divided palladium deposited on asbestos fibers. It was prepared as follows: One gram of acid washed asbestos fiber was impregnated with a solution of one gram of palladium chloride in 2 cc. of HCl (Sp. Gr. 1.19) and 8 cc. of water. The mass was then mixed thoroughly with 2 cc. 37% formaldehyde solution followed by 15 cc. of 10% sodium hydroxide. The palladium chloride was reduced according to the following equation:

$$3NaOH + HCHO + PdCl_2 \rightarrow Pd + NaOOCH + 2NaCl + 2H_2O$$

The mass was then filtered, washed twice with water, twice with 10 cc. portions of 20% acetic acid, and again with water until neutral. After drying at 95°for two hours, the catalyst was ready for use.

No definite apparatus was outlined by Littman (3) for carrying out the dehydrogenation of abietic acid. The apparatus outlined on the following page was designed and constructed by



Catalyst Support ~ 8mm rod with projections of 4mm rod
Reaction Tube ~ 42 mm. pyrex tube
Oil Bath ~ 4½ in. iron pipe

the author. It was found to give excellent results for charges of abietic acid up to 200 grams.

The catalyst was draped over the glass support so that it was evenly distributed throughout the large test tube immersed in the oil bath. The abietic acid was then warmed, poured into the tube and heated for one hour at 230°. Agitation was secured by convection currents. At the end of the reaction period, the product was poured off from the catalyst and any solid material removed from the product by filtration. The product was then distilled at 2-3 mm. to remove any colored impurities.

The product was crystallized from acetone, using 1.3 grams of acetone per gram of solid material. After cooling the crystals were washed with cold acetone and air dried.

Three runs were made according to this proceedure, and the following results were obtained:

Preparation of Dehydroabietic Acid

No.	m.p.	Abietic Acid Used		Yield in Grams	% Yield
1.	163-66°	No. 1	170 Gms.	69	40.8%
2.	165-66°	No. 2	120 Gms.	32	26.9%
3.	163-65°	No. 3	170 Gms.	49	29.1%

No explanation can be offered for the variation in yields.

BROMINATION OF DEHYDROABIETIC ACID

Nine efforts were made to brominate dehydroabietic acid. Although no definite bromination compound was obtained, the following outline of each effort may be enlightening:

I

Five grams of dehydroabietic acid No. 1 (see table on page 8) were dissolved in the least amount of carbon tetrachloride and treated with twice the theoretical amount of bromine for the formation of the dibromo derivative. Iron was used as a catalyst. Reaction started at slightly above room temperature and proceeded violently with the evolution of hydrobromic acid. The reaction was allowed to proceed until there was no further evidence of reaction. The mixture was then heated on the water bath for half an hour. No crystals formed on cooling to room temperature. Further cooling in an ice bath produced no crystals. The product was then poured into ice water and a gummy material separated. A small quantity of dilute KOH was added to remove excess bromine. The gummy material was separated and attempts were made to crystallize it from acetone, carbon tetrachloride, ethyl alcohol, ether, ligroin and methyl alcohol. No crystals were obtained from any of these solvents.

II

Five grams of dehydroabietic acid No. 1 were treated in the same manner as in I. At the end of the reaction the solvent was evaporated from the mixture. After an unsuccessful attempt

to crystallize the residue from acetone was made, the solvent was again evaporated and the material dissolved in KOH. It was not possible to reprecipitated the material from solution with dilute HCl.

III

Five grams of dehydroabietic acid No. 1, dissolved in carbon tetrachloride, was treated with bromine in the presence of iron. The reaction was allowed to proceed at room temperature for 48 hours. Hydrobromic acid was still being given off at the end of this period. The mixture was then heated over a water bath for half an hour. The solution was washed with 10% Na_2CO_3 solution. The solvent was evaporated, the residue dissolved in CH_3OH and this solution poured into cold water. An attempt to crystallize this material from a CH_3OH-water mixture yielded an extremely small amount of crystals, m. p. 187-89°. The quantity of crystals obtained was too small to permit an analysis of any sort.

IV

Five grams of dehydroabietic acid No. 1, dissolved in carbon tetrachloride, were treated with bromine in the presence of tin. The reaction was allowed to proceed at room temperature for two hours, then the mixture was heated to the full heat of a water bath for two hours. The solvent was evaporated and the residue dissolved in CH_3OH. No crystals were formed on cooling to -20°C. An attempt to recover the precipitate from this solution resulted in the formation of an unworkable gum.

V

Five grams of dehydroabietic acid No. 1, dissolved in CH_3OH, was treated with bromine in the presence of iron. The reaction was allowed to proceed at room temperature for two hours. The reaction mixture was poured into cold water, the solid material filtered and again dissolved in CH_3OH. No crystals could be obtained by crystallizing from methyl alcohol, ethyl alcohol, acetone or carbon tetrachloride.

VI

Twenty five grams of dehydroabietic acid No. 1, dissolved in CCl_4, was treated with bromine in the presence of iron. The reaction was allowed to proceed at room temperature over night and continued at the full heat of a water bath for two hours and a half. The carbon tetrachloride was removed by evaporation and the residue dissolved in CH_3OH. A small quantity of crystalline product was obtained, m. p. 170-75°. This could have been some of the original dehydroabietic acid. The quantity of crystals was again too small to permit analysis.

VII

Ten grams of dehydroabietic acid No. 1 was subjected to the same treatment as in VI. No crystals were obtained from various solvents.

From these experiments it appears that either no bromo product is formed or the product formed is not of a crystalline nature. If the latter is assumed to be the case, it might be possible to hydrolyze the product and obtain a more easily workable product which would give some indication of what had taken

place in the bromination reaction. Two more experiments were carried out to test this assumption.

VIII

Ten grams of dehydroabietic acid No. 2, dissolved in the smallest possible quantity of carbon tetrachloride, was treated with bromine in the presence of iron. The reaction was allowed to proceed at room temperature over night and then continued for two hours at the full heat of a water bath. The carbon tetrachloride was removed by evaporation and the residue dissolved in CH_3OH. This solution was poured into cold water. The precipitate was filtered, washed well with water and refluxed for three hours in a 10% solution of Na_2CO_3. The precipitate was only slightly soluble in Na_2CO_3. The precipitate was filtered, washed and dried. A test for bromine was negative. There was no evidence of reaction with acetic anhydride or acetyl chloride.

IX

Ten grams of dehydroabietic acid No. 2 was treated as in VIII. The precipitate obtained was refluxed with 10% KOH solution for 12 hours. The precipitate was completly soluble in the KOH solution. The acid material was precipitated with 6N HCl and separated by filtration. The precipitate gave no test for bromine and there was no indication of a reaction with acetic anhydride or acetyl chloride.

NITRATION OF DEHYDROABIETIC ACID

The method suggested by Fieser and Campbell (2) was chosen for the preparation of dinitrodehydroabietic acid. Five grams of dehydroabietic acid No. 2 was mixed slowly with a mixture of 30 cc. of H_2SO_4 and 20 cc. HNO_3 which had been cooled in an ice bath. The mixture was allowed to come to room temperature, then poured into a liter of cold water. The precipitate was filtered and crystallized from acetone. A product, m. p. 165-69°, was obtained. This agreed well with the dinitrodehydroabietic acid prepared by Fieser and Campbell (2).

In attempting to reduce one of the nitro groups, the following proceedure was used: The dinitrodehydroabietic acid was dissolved in hot C_2H_5OH (a quantity such that on cooling, a fine suspension of crystals resulted). Five cc. 15N NH_4OH was added and H_2S passed through the solution for half an hour. The mixture was then poured into a liter of cold water. The precipitate was filtered and digested with HCl. No acid soluble substance was obtained. Acetone extraction and crystallization gave the original product.

This experiment was repeated with identical results, showing that dinitrodehydroabietic acid cannot be partially reduced by this method.

SUMMARY

Abietic acid and dehydroabietic acid were prepared from Hercules Commercial Abietic Acid by accepted methods.

Attempts to isolate a bromination product or to show evidence of bromination were unsuccessful. The experiments indicated that a variety of decomposition products were formed. A study of these decomposition products might prove interesting.

It has been shown that the reduction of one or both of the nitro groups of dinitrodehydroabietic acid was not possible with the use of $(NH_4)_2S$.

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(1) Steele, J. Am. Chem. Soc., 44, 1333, (1922).

(2) Fieser and Campbell, J. Am. Chem. Soc., 60, 159, (1938).

(3) Littman, J. Am. Chem. Soc., 60, 1419, (1938).

(4) Hasselstrom and Campbell, J. Am. Chem. Soc., 60, 2340 (1938).

(5) Fieser and Campbell, J. Am. Chem. Soc., 60, 2631, (1938).